



Influence of molecular weight on the properties of poly(ether ether ketone)

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Variations in molecular weight of poly(ether ether ketone) significantly alter its processing behavior, product properties, and performance.

Poly(ether ether ketone) (PEEK) has generated interest in many fields. The electronics, health-care, and aerospace industries, for example, have found applications for PEEK because of its exceptional chemical, radiation, wear, and abrasion resistance, high mechanical strength, and heat-distortion temperature.¹ The effects of molecular-weight variations on the thermal, mechanical, and rheological behavior of PEEK have received relatively little attention, despite important implications for many other engineering and high-performance polymers also bearing primarily aromatic backbones.

Here, we report our findings on the effects of varying the molecular weight of PEEK on its physical properties. We used molecular weights (measured by size-exclusion chromatography) of 23,000, 27,000, and 37,000g/mol, corresponding to 80, 94, and 129 repeat units (designated PEEK80, PEEK94, and PEEK129, respectively). We characterized the thermal behavior of these different polymer grades using differential-scanning-calorimetric analysis. Both isothermal and nonisothermal crystallization processes resulted in a crystallization index for all three grades of approximately 3.0, indicating a tendency for all to form spherulitic crystals. The material's melting temperature and crystallinity decreased slightly with increased molecular weight, while the crystallization temperature decreased dramatically. We determined isothermal crystallization-activation energies of -565, -553, and -408kJ/mol for PEEK80, PEEK94, and PEEK129, respectively. We obtained comparable values from our nonisothermal crystallization-activation study. This data suggests that, compared to commodity polyolefin resins, PEEK has a much faster rate of crystallization.² However, the rate greatly decreases with increasing molecular weight. These molecular-weight-dependent relationships should be considered when determining how to process PEEK to obtain the most desirable product.

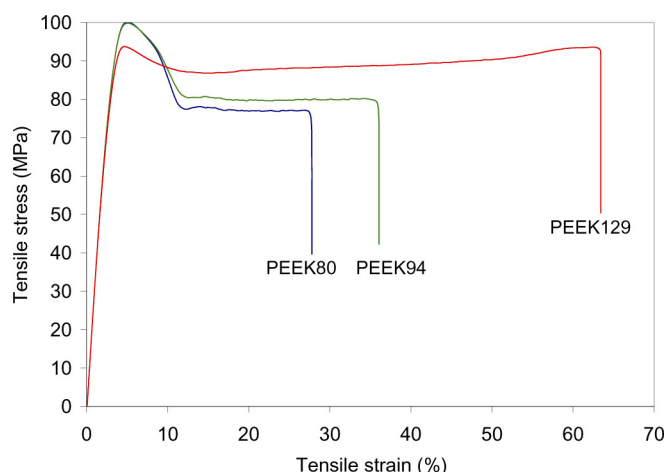


Figure 1. Stress-strain curves for poly(ether ether ketone) (PEEK) polymers of differing molecular weight. PEEK80: 23,000, PEEK94: 27,000, and PEEK129: 37,000 g/mol.

The performance of PEEK-based products depends on the polymer's mechanical and thermomechanical behavior. We conducted dynamic-mechanical thermal analysis, in addition to tensile and impact tests, to assess the effects of molecular-weight variations on these properties. In the low-temperature region, the storage moduli for all three grades of PEEK were comparable, while high-molecular-weight PEEK demonstrated a slightly smaller flexural modulus than the low-molecular-weight polymers. In the glassy region and in the rubbery phase above the glass-transition region, the storage moduli significantly decreased with increasing polymer molecular weight. In addition, as molecular weight increased, the tensile strength at yield decreased, while that at break increased. As molecular weight of PEEK increased, the tensile moduli decreased slightly, while the tensile strain increased greatly (see Figure 1).

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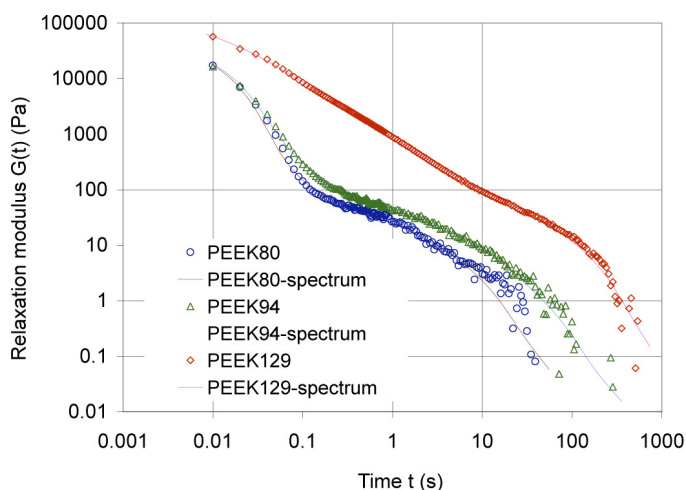


Figure 2. Stress-relaxation curves of PEEK polymers of differing molecular weight at 380°C. Open circles, triangles, and diamonds: Experimental data. Solid lines: Relaxation-curve best-fitting spectra.

Many aspects of PEEK processing and performance behavior are related to its relaxation characteristics, which have not previously been reported. Our relaxation study of PEEK, using a parallel-plate rheometer, demonstrated that a slight increase in molecular weight can significantly increase the relaxation time: PEEK129 exhibited relatively linear behavior, analogous to rubber-type relaxation (see Figure 2). However, PEEK80 and PEEK94 have at least two different relaxation regions.

We conducted rheological studies using a capillary rheometer in steady shear mode and a parallel-plate rheometer in both steady and dynamic modes. The broad range of shear rates from these experiments encompassed conditions relevant to PEEK melt processing, secondary operations, and stress relaxation. In the entire shear-rate region studied, the shear viscosity increased dramatically with increased molecular weight (see Figure 3). Additionally, double-shear-thinning behavior, analogous to that of liquid-crystalline polymers, distinguishes PEEK from many other polymers. We determined the double-melt shear-thinning regions of PEEK. In low-frequency regions, it can be assigned to molecular relaxation at crystalline interfaces and is related to the double-melt-peak phenomenon of PEEK.

In summary, understanding the influence of molecular weight on the PEEK thermal, mechanical, and rheological behavior, and product performance will be useful for optimization of product development. Additionally, both primary and secondary conversion processes (such as injection molding and extrusion on the one hand and annealing and post-processing on the other) will benefit from this work. This represents one direction in our continuing efforts to better understand engineering and high-performance polymers. Ultimately, the design of

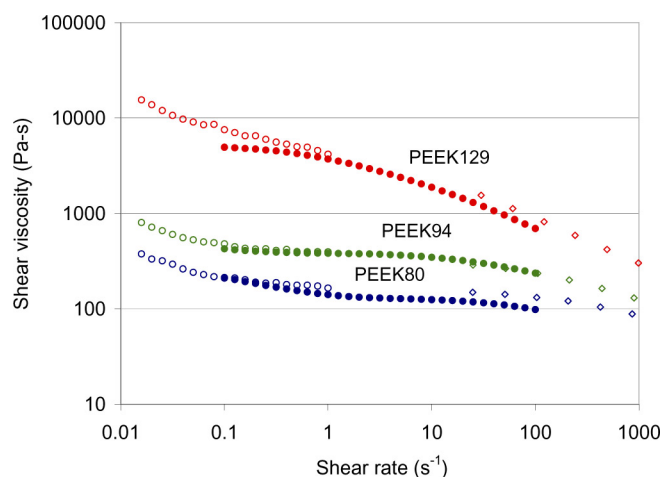


Figure 3. Shear viscosity of PEEK polymers of differing molecular weight. Open, solid circles: Parallel-plate rheometry data in steady-state ($0.01\text{--}1.0\text{s}^{-1}$) and dynamic mode ($0.1\text{--}100\text{rad/s}$), obtained based on application of the Cox-Merz rule. Open diamonds: Capillary rheometry data ($50\text{--}1000\text{s}^{-1}$).

high-performance PEEK composites will be optimized because of an understanding of these molecular-weight/performance trends.

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